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Chapter 7: Evaluation of Analytical Methods for the Detection of Ethanol in Ground and Surface Water

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7.1. Analytical Requirements

7.1.1. Routine Detection of Trace Amounts of Ethanol in Environmental Waters

Ethanol in the environment might be present in air, soil, and water. Ethanol in air partitions to water[1]. In an organic soil/water system, ethanol partitions almost exclusively into the water[2]. Thus, water is an important environmental reservoir for ethanol. The primary objective of this chapter is to review methods applicable to the routine analysis of ethanol in environmental waters. (The analysis of ethanol in air and soil is outside the scope of this document and will not be addressed.)

The analysis of ethanol in environmental waters is difficult. In order to analyze ethanol, or any other contaminant of interest, one must first extract (or remove) it from water. Once it is removed from water, the contaminant must then be separated from hundreds or thousands of other contaminants so that it can be specifically identified or detected. Once it has been identified, the quantity of that contaminant in the water can be determined. Of these steps, the extraction of ethanol from water is the most challenging.

Ethanol is a small, polar molecule. Ethanol associates (or hydrogen bonds) with water, making it difficult to extract from water and difficult to measure low concentrations in the environment. However, if ethanol can be extracted from water, sufficient methods exist to separate, identify, and measure it.

The appropriate analytical methods to analyze (that is, extract, separate, identify, and measure) ethanol, or any other environmental contaminant, are dictated by the intended use of data. This review considers three uses of collected data:

- Assessment of ethanol concentrations at a spill site.
- Documentation to meet regulatory requirements.
- Understanding of the environmental fate and transport of ethanol.

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[1] Based on accepted values of Henry's law constant for ethanol that range from 0.5 to 0.6 Pa•m^3/mol (MacKay, *et al.,* 1995).

[2] Ethanol's low octanol-water partition coefficient (K_{OW}), log K_{OW} values of –0.3 to –0.2 (MacKay *et al.,* 1995) indicate that ethanol partitions into water rather than remaining in soil.

Several issues influence the selection of an analytical method that will provide the data needed for these three uses. In all cases, the selected analytical methods must possess the following characteristics:

- Appropriate DLs.[3]
- Good precision.[4]
- Good accuracy.[5]
- Easily performed and reproducible by different analysts in different laboratories.
- No false positive (interferences) or negative detections.
- Adherence to quality assurance/quality control (QA/QC) protocols.[6]

For any type of chemical analysis, adherence to stringent QA/QC protocols is the criterion most critical to providing data that can be compared by different investigators. It is for this reason that the United States Environmental Protection Agency (US EPA) has promulgated specific analytical methods (and strict QA/QC protocols) for the monitoring of contaminants in the environment. For example, all laboratories performing regulatory analyses must strictly adhere to the US EPA protocols to prove regulatory compliance.

Another issue of concern is practicality. The chosen analytical methods need to be cost effective and easily performed (with minimal manual labor). Costs of current analyses for organic compounds range from approximately $100–$400. Thus, in order to be cost effective, analyses of environmental samples for the presence of ethanol should fit into this price range.

7.1.2. Regulatory Requirements Versus Detection Limits for Fate and Transport Studies

We previously stated that there are several reasons that one might wish to monitor ethanol contamination in the environment, including (1) to assess ethanol contamination at a spill site, (2) to document that regulatory requirements are being met or exceeded, and (3) to understand the environmental fate and transport of ethanol. In each case, it is important to establish what concentration of ethanol needs to be detected in order to meet the objective of the study.

For example, a regulatory concentration limit for a specific contaminant might be based on predicted health effects and risk-assessment models. Let's assume that the regulated limit of Analyte X is 30 parts-per-billion (ppb) in drinking water. In order to prove that the regulatory concentration of Analyte X is not exceeded, the method selected to analyze drinking water must be capable of accurately and reproducibly measuring 30 ppb of ethanol. Thus, the DL (or the minimum concentration of Analyte X that can be detected by an analytical method) required for this analysis is 30 ppb or lower. In practice, the desired detection limit (DL) should be three to

[3] The analyte must be detected at a sufficiently low concentration to meet the study/regulatory requirements.

[4] Multiple measurements of an analyte in the same sample will give identical results.

[5] Measured concentration of analyte reflects its true concentration in a sample.

[6] A QA/QC program encompasses procedures used to ensure that analyses are consistently performed, meet user requirements, and that data generated by a laboratory are accurate, precise, reproducible, and defensible in a court of law.

five times lower (6–10 ppb) than the set regulatory limit desired in order to ensure that Analyte X is easily detected at its regulated limit of 30 ppb.

Currently, ethanol is not considered by the federal government or by the state of California to be a regulated compound. No guidance is available to dictate needed DLs. However, based on the potential uses of ethanol data, we can make some good assumptions about what DLs are needed to provide data for specific studies:

- **Case 1: Assessing Ethanol Contamination at a Spill Site.** The expected concentration of ethanol in contaminated groundwater near a spill site is likely to range between 400 to 4000 parts per million (ppm) (Malcolm Pirnie, Inc., 1998). Thus, the monitoring of ethanol-contaminated water associated with fuel spills would require methods with DLs of 400 ppm in order to document significant ethanol contamination at a site. In addition, the selected analytical method must detect ethanol in the presence of high concentrations of hydrocarbons found in gasoline.
- **Case 2: Documenting That Regulatory Requirements Are Met.** The taste and odor thresholds of ethanol in drinking water are 50 ppm and greater than 100 ppm, respectively (Malcolm Pirnie, Inc., 1998). If we assume that no adverse health effects are associated with consuming trace quantities of ethanol, we would predict that a drinking-water standard would be set at the taste threshold of ethanol (50 ppm). Thus, a method at least 50 ppm would be sufficient to ensure water quality. This DL is approximately a factor of ten lower than that required to characterize ethanol contamination at a spill site.
- **Case 3: Understanding Environmental Fate and Transport.** In order to determine the movement of ethanol through the environment, the environmental background levels of ethanol at uncontaminated sites need to be assessed. Parts-per-billion concentrations of ethanol, possibly produced by "natural" chemical and biological processes, might be present in environmental surface and groundwaters. It is also possible that surface and groundwaters will be indirectly impacted by the use of blended fuels. In order to understand the native background of ethanol in the environment and to understand the impact of ethanol from blended fuels, the lowest DLs achievable (parts per billion, or better) would be needed.

7.2. Evaluation of Current Analytical Methods for Ethanol Detection

Few papers have been published describing the analysis of ethanol in environmental samples. This pretermission is, in part, because ethanol has not been considered to be a contaminant of environmental concern. Ethanol is not included in several comprehensive references of groundwater contaminants (Prager, 1995; Montgomery, 1996). In addition, because the human body tolerates percent quantities of ethanol that are present in alcoholic beverages, human consumption of trace quantities of ethanol, which might contaminate food and drinking water, have not been of great concern.

7.2.1. Ethanol Analysis Methods Used by Food and Biomedical Industries

Table 7-1 summarizes the methods that have been used for ethanol analyses. It also contains information about the analytical technique applied, the type of sample analyzed, and the limit of detection obtained. It also indicates if the method might be useful in the analysis of environmental waters.

The alcoholic beverage industry performs many ethanol analyses to insure the quality of its products. Ethanol DLs for the analyses of beer and wine cited in Table 7-1 range from 1 to 50,000 ppm. However, many of these methods do not have sufficient DLs to be applied to the analysis of ethanol in environmental samples. The method using an oxygen-electrode sensor (5–10 ppm DLs) lacks a large dynamic range and would not be applicable to environmental analyses. The gas-diffusion membrane coupled with amperometric detection (1-ppm DL) might prove useful for the analysis of environmental samples; however, studies need to be performed to determine if this method is applicable to environmental samples.

DLs for ethanol in biological fluids reported within the last five years are 10 ppm or better (see Table 7-1). Note that these DLs are below the taste and odor thresholds for ethanol in water. The recent methods cited used either headspace gas injection or direct injection of the biological fluid coupled with gas chromatography combined with flame-ionization detection (GC/FID). GC/FID is more analyte specific than many of the electrochemical methods used in the alcoholic beverage industry. Because of their good DLs, GC/FID methods are potentially applicable to the analysis of ethanol in environmental samples.

7.2.2. Ethanol Analysis Methods Used by the Environmental Community

In 1986, the United States Environmental Protection Agency (US EPA) suggested that ethanol analysis might be performed by purge-and-trap gas chromatography coupled with a flame-ionization detector (that is, Method 8015 [US EPA, 1986]). Method 8015 listed no method DL, linear range, precision, or accuracy data. By 1996, both US EPA Methods 8015B and 8260B stated that purge-and-trap extraction was inappropriate for ethanol analysis (US EPA, 1996c and 1996d). Instead, these methods suggested that azeotropic distillation (that is, Method 5031 [US EPA, 1996a]) and vacuum distillation (Method 5032 [US EPA, 1996b]), were appropriate techniques to extract and concentrate ethanol from water samples. In addition, these methods suggested that direct aqueous injection of water into a GC/FID, or the use of a gas chromatograph coupled with a mass spectrometer (GC/MS) was appropriate for ethanol analysis. Again, because ethanol is not a regulated compound, the US EPA methods contained no information regarding DL, linear range, precision, or accuracy.

While the US EPA does not endorse the use of the purge-and-trap technique for ethanol analysis, several methods have successfully used this extraction technique. *Geo*Chemistry of Canoga Park, CA (recently purchased by and soon to relocate to ZymaX Envirotechnology, Inc., of San Luis Obispo, CA) is one of the few California laboratories known to perform ethanol analyses for environmental samples. Global *Geo*Chemistry (1999) uses a modified version of Method D4815 of the American Society of Testing and Materials (ASTM, 1997) to determine ethanol in aqueous samples. ASTM Method D4815 was developed to measure

0.1% concentrations of ethanol in gasoline and uses two-dimensional gas chromatography (2D-GC) to remove interferences. The sample is injected directly into the gas chromatograph and first eluted through a polar, capillary gas-chromatograph column that retains all oxygenates, including ethanol. The oxygenates are then backflushed into a nonpolar, capillary gas-chromatograph column for final separation and detection by a flame-ionization or thermal-conductivity detector.

The Global *Geo*Chemistry method combines purge-and-trap extraction with two-dimensional chromatography coupled with a flame-ionization detector. DLs for ethanol in clean water and in water contaminated with 5% nonaqueous phase liquid (NAPL) are 200 ppb and 100 ppm, respectively.[7]

Zymax Envirotechnology, Inc. (McMurphy, 1999) has modified US EPA Method 8260B to obtain 50-ppb DLs for ethanol in water. Its method uses purge-and-trap extraction at ambient temperature and cryofocussing prior to final analysis by GC/MS[8].

Researchers at the University of Nebraska have developed a solid-phase microextraction (SPME) method coupled with GC/MS for the determination of ethanol in water. The SPME method uses a small fiber (~1 cm in length by ~0.3 mm in diameter), which is coated with 85 μm of a carboxen/polydimethylsiloxane polymer, to extract ethanol from water. After it has soaked in the sample for about 30 minutes, the fiber, now containing ethanol, is removed from the sample and directly injected into a GC/MS so that the amount of ethanol that has been collected can be measured. This method yields DLs for ethanol of 15 ppb (Cassada *et al.*, 1999). This represents the best DL that has been reported to date for the determination of ethanol in water. Although SPME can be automated easily, this technique requires a greater level of expertise to perform than purge-and-trap methods.

7.3. Handling and Preservation of Ethanol Samples

In addition to the instrumentation used for ethanol analysis, researchers must consider sample collection, preservation, and storage. If a sample is not properly collected, preserved, and stored, then the data provided by sample analyses will be of questionable quality and will not be scientifically (or legally) defensible.

Little has been reported regarding the collection and preservation of samples containing ethanol. The conventional US EPA methods for sample collection and storage are often applied, even though the storage methods endorsed have not always been rigorously tested. The US EPA recommends collecting water samples in 40-milliliter (mL), glass vials with Teflon®-lined

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[7] Sample matrix affects DLs. In general, DLs will increase, or worsen, as the complexity of the sample matrix increases. In a complex matrix, many compounds are present at much higher concentrations than the compound of interest, and these other compounds can interfere with the analytical signal produced by the compound of interest. To obtain the best DLs possible, analysts must separate ethanol from other unknowns that might interfere with its detection.

[8] For optimal gas chromatographic (GC) analysis, it is necessary to introduce the analytes as a narrow band on the head of the GC column. In practice, very volatile compounds, such as ethanol, often "smear" at the head of the GC column. One method to reduce this band broadening is to cool the GC column to sub-ambient temperatures (or, to temperatures that are below the boiling points of the analytes). This, in effect, traps (or focuses) volatile compounds as a narrow band of liquid at the head of the GC column and affords optimal GC analysis.

septum caps. No headspace should be visible in the vials after sample collection. The samples should then be stored at 4°C for a maximum of 14 days prior to analysis. To help preserve water samples and to minimize bacterial growth that might degrade analytes in the sample, four drops of concentrated hydrochloric acid may be added prior to cooling (Keith, 1996). In accordance with US EPA-recommended procedures, Global *Geo*chemistry (1999) refrigerates water samples but does not preserve them with acid.

Researchers working on samples of biological fluids have also refrigerated samples prior to analysis. McCarver-May and Durisin (1997) stored blood at 4°C prior to analysis. According to Macchai *et al.* (1995), ethanol was stable for seven days in urine, serum, plasma, and saliva when stored at 4°C; and ethanol in these matrices was also stable for up to two years when stored at -20°C. Tangerman (1997) observed that ethanol in blood was stable for two weeks when stored at room temperature, refrigerated, or frozen. Water, blood, serum, and urine samples containing ethanol could be stored for three months at -20°C without ethanol loss (Tangerman, 1997).

7.4. Recommendations to Improve Sampling and Analysis of Ethanol in Ground and Surface Water

7.4.1. Rigorous Study of Sample Preservation

The best conditions for the preservation and storage of samples containing ethanol need to be determined. The commonly used protocol of collecting water samples in 40-mL vials with Teflon®-lined septum caps and with no headspace should be continued. Data from the biomedical community appears to validate the commonly used practice of storing aqueous samples at 4°C for up to 14 days prior to analysis. Because the biomedical community suggests that frozen samples containing ethanol can be stored for periods as long as two years, it is possible that, under certain conditions, samples collected for ethanol analysis can be stored longer than 14 days prior to analysis. It will be important to determine if environmental samples can be stored for long periods without loss of ethanol.

7.4.2. Improved Extraction of Ethanol from Aqueous Samples

The analysis of ethanol in environmental waters is difficult. As previously discussed, ethanol is a small, polar molecule and is difficult to remove from water. The poor extraction efficiency of ethanol from water is the main contributor to its poor analytical DLs. Thus, any improvements in methods to remove ethanol from water will result in better DLs. The literature reviewed for this study indicates that either direct injection of an aqueous solution or injection of the headspace above an aqueous liquid can be used to obtain DLs of 10 ppm or less. Thus, these sample introduction techniques are sufficient to detect ethanol at its taste or odor threshold. Both of these techniques are easy and inexpensive to perform.

Other sample introduction techniques, such as purge and trap, azeotropic distillation, or vacuum distillation, could be investigated in the search for lower ethanol DLs. Of these techniques, azeotropic distillation and vacuum distillation are more expensive and labor-intensive (and not often performed) than purge and trap, which is performed easily, cost-effectively, and routinely by contract laboratories. The newer technique of solid-phase

microextraction (Zhang, 1994), in which ethanol might be removed from water using a small fiber coated with special material, might also merit investigation. However, solid-phase microextraction is not currently performed routinely by contract laboratories.

7.4.3. Improved Strategies for Ethanol Detection

In order to eliminate problems with potential interferences, we recommend that gas-chromatographic (GC) separation be used in all future ethanol analyses. There are two practical strategies that can be used for the sensitive detection of ethanol in the presence of interfering compounds. The first is to use the best possible gas-chromatography procedure to separate ethanol from any interferences and, then, to detect ethanol with a nonspecific detector, such as a flame-ionization detector. The second strategy is to perform a less rigorous gas-chromatographic separation coupled with a detector that would respond specifically to ethanol but would not respond to potentially interfering compounds. Both of these strategies merit consideration.

7.4.3.1. Use of Gas Chromatography and Nonselective Detector

In the literature reviewed, flame-ionization detectors (FIDs) were the detectors of choice for ethanol analysis. A FID is frequently used because it responds well to a variety of organic compounds. Because of the nonselective nature of the FID (that is, the FID provides a signal whenever an organic compound is detected and provides no information about the nature of that analyte), two-dimensional chromatography is recommended for use with this detector to minimize interferences.

7.4.3.2. Use of Gas Chromatography with an Analyte-specific Detector

To improve detection specificity, we recommend investigating the coupling of a gas chromatograph with an analyte-specific detector, such as either an atomic-emission detector (AED) or a mass spectrometer (MS). The AED, operated in the oxygen-specific mode, can be "blinded" to potentially interfering hydrocarbons. The MS is capable of providing a mass-spectral "fingerprint" unique to each organic compound. Neither the AED nor the GC/MS would be cost prohibitive for an environmental laboratory to purchase, staff, or maintain. It might be possible that use of the AED or MS would simplify the chromatographic requirements such that only one GC column would be required to separate ethanol from potential interferences.

7.4.4. Minor Modifications to Improve Existing Methods

In addition to the choice of experimental approach and instrumentation used for ethanol analysis, there are several other analytical aspects to consider. Minor modifications to existing methods might improve the detection of ethanol in water. For example, if conventional purge-and-trap extraction is to be used, the sample could be heated to improve ethanol extraction efficiency. The choice of GC column dictates how efficiently ethanol can be separated from interferences. Many different types of GC columns are available and could be tested for their applicability to ethanol analysis. The use of cryofocussing in combination with gas chromatography might be beneficial.

7.5. Summary

The literature reviewed indicates that the technology currently exists to enable researchers to detect ethanol at spill sites. Sufficient methods exist to determine ethanol at its taste threshold of 50 ppm in water. The implementation of these methods would require some study of extraction and detection conditions and the establishment of strict QA/QC protocols. These are of great importance in the development of a method that would be used to demonstrate regulatory compliance. No methods reported are currently able to detect ethanol below 15 ppb in water. Thus, much time and effort must be invested to enable the detection of trace concentrations of ethanol. Until this is accomplished, we will be unable to completely understand the fate and transport of ethanol in the environment. Regardless of the analytical methods selected for use, it is recommended that a proposed method be evaluated using a variety of sample matrices—a strategy that has been used previously to evaluate detection methods for methyl tertiary butyl ether (MBTE) and other gasoline oxygenates (Happel *et al.*, 1998).

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Table

Table 7-1. Summary of ethanol methods. Data are ordered by publication date and subgrouped by decreasing limit of detection.

Technique	Sample	Limit of detection (ppm)	Useful in environmental analysis?	Reference
Headspace GC/FID	plasma	1000	no	Watts and McDonald, 1990
Derivatization to ethyl dithiocarbonate; differential-pulse polarography	beer	200	no	Chan *et al.,* 1992
Oxygen electrode based on NADH oxidase from *Bacillus licheniformis* and alcohol dehydrogenases	wine	5–10	no	Ukeda *et al.,* 1993
Online, membrane inlet ion mobility spectrometry	beer	500	no	Kotiaho *et al.,* 1995
Heated (75°C) headspace GC/FID	biol. fluids	10	maybe	Macchia *et al.,* 1995
Flow injection analysis coupled with gas-diffusion membrane and immobilized alcohol oxidase; amperometric detection	beer, wine	1	maybe	Mohns and Künnecke, 1995
Micellar electrokinetic capillary chromatography; diode-array detection	wine	50,000	no	Collins *et al.,* 1997
Solid-phase extraction cleanup; flow-injection analysis; amperometric detection	wine	500	no	Chen *et al.,* 1997
Heated (75°C) headspace GC/FID	blood	0.3	yes	McCarver-May and Durisin, 1997
10-microliters (-µL) direct injection, GC/FID	biol. fluids	0.1	yes	Tangerman, 1997
5-µL direct injection, GC/FID	water	3	yes	Corseuil *et al.,* 1998
5-µL direct injection, GC/FID	water	1	yes	Alvarez, 1999
Modified ASTM Method D4815 (purge & trap, 2D GC/FID)	soil, water	0.2	yes	Global *Geo*Chemistry, 1999
Modified US EPA Method 8260B with cryofocussing	water	0.05	yes	McMurphy, 1999
Solid-phase microextraction coupled with GC/MS	water	0.015	yes	Cassada, *et al.,* 1999

Key:

2D-GC = two-dimensional gas chromatography

ASTM = American Society of Testing and Materials

US EPA = United States Environmental Protection Agency.

GC/FID = gas chromatography with flame-ionization detection

GC/MS = Gas chromatograph with a mass spectrometer.